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Application Serial No. 10/627,945

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:	)	
	)	
Dennis J. Jones, Jr.	)	Art Unit: 1751
	)	
Application No.: 10/627,945	)	Examiner: Ogden, Jr., N.
	)	
Filing Date: July 24, 2003	)	Confirmation: 3664
	)	
For: "METHODS OF TREATING AND	)	
CLEANING FIBERS, CARPET YARNS AND	)	
CARPETS"	)	

**DECLARATION UNDER 37 C.F.R. § 1.132 OF DENNIS J. JONES, JR.**

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February 22, 2007

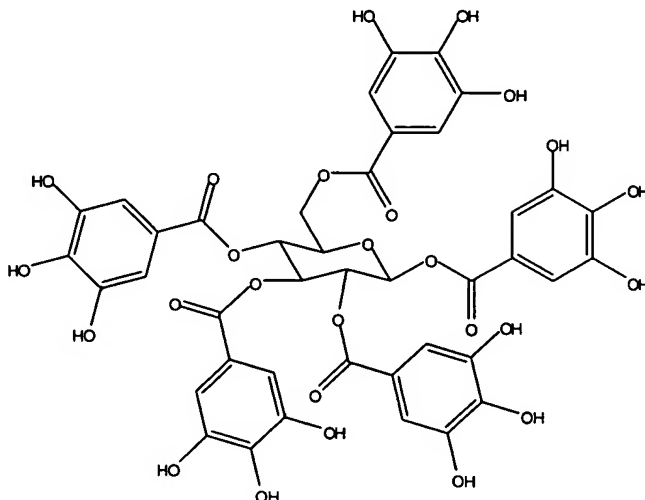
Sir:

The undersigned, Dennis J. Jones, Jr., a citizen of the United States, residing at 18 Ridge Rock Drive, Signal Mountain, Tennessee 37377, declares that:

1. I am the inventor listed on the above-identified application.
2. I hold a Bachelor of Science degree with a Biology major and Chemistry minor from the Berry College in Rome, Georgia and a Master of Science (undesignated) with studies in textile science from the Georgia Institute of Technology in Atlanta, Georgia.
3. I have been conducting research in the fields of textile science and engineering with emphasis on carpet manufacturing for twenty-five years, from 1981 to the present, and am listed as an inventor on at least three issued U.S. patents and at least five pending patent applications relating to carpet manufacture, carpet dyeing, and/or carpet protective treatment systems in general.



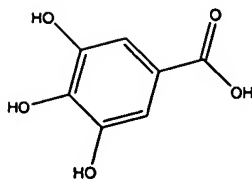
4. From June 1981 to the present, I have been employed in Dalton, Georgia as Director of Manufacturing Technical Resources for Shaw Industries, Inc., the largest carpet manufacturing company in the world.
5. As described in THE MERCK INDEX: AN ENCYCLOPEDIA OF CHEMICALS, DRUGS, AND BIOLOGICALS, THIRTEENTH EDITION 1615-16 (Maryadele J. O'Neil *et al.* eds., 2001) and HAWLEY'S CONDENSED CHEMICAL DICTIONARY 1067-68 (14<sup>th</sup> ed. 2001) (copies are attached hereto), tannic acids are well known in the art and comprise compounds derived from nutgalls having a structure of polygalloylglucose or polyalloylquinic acid. The sugar residue can be substituted with one or more residues of gallic acid, digallic acid, and/or trigallic acid. Tannic acid can have, for example, the following structure:



Note specifically the multiple ester functionalities that bind the gallic acid residues (carboxylic acid) to the sugar residue (alcohol) to form a tannic acid.

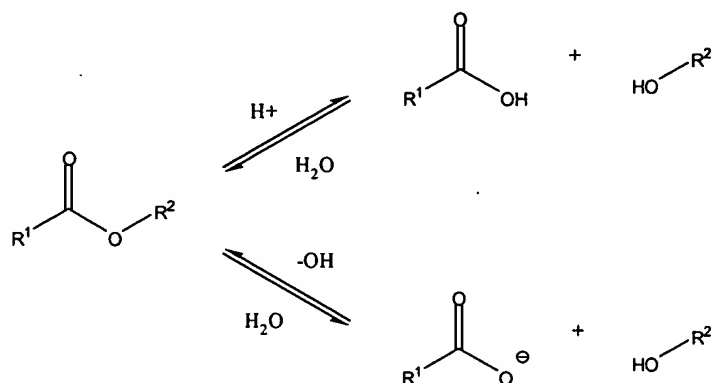
6. As described in THE MERCK INDEX: AN ENCYCLOPEDIA OF CHEMICALS, DRUGS, AND BIOLOGICALS, THIRTEENTH EDITION 772 (Maryadele J. O'Neil *et al.* eds., 2001) and HAWLEY'S CONDENSED CHEMICAL DICTIONARY 524 (14<sup>th</sup> ed. 2001) (copies are attached hereto), free gallic acid (3,4,5-trihydroxybenzoic acid) is one component of tannic acid that can be present in commercially-available tannic acids and has the following structure:





Note specifically that gallic acid is a carboxylic acid.

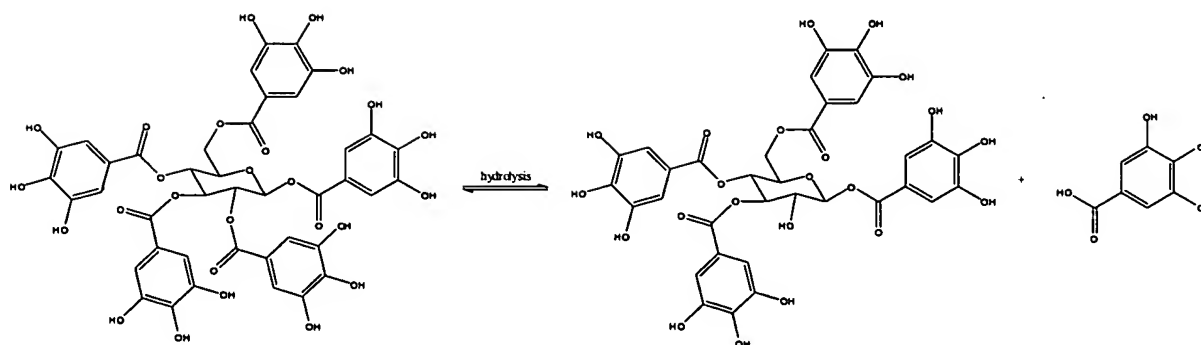
7. As described in J. March, ADVANCED ORGANIC CHEMISTRY: REACTIONS, MECHANISMS, AND STRUCTURE, THIRD EDITION 334-35 (1985) (a copy is attached hereto), ester hydrolysis is usually catalyzed by acids or bases and transforms a carboxylic acid into its constituent carboxylic acid (or salt thereof) and alcohol:



Thus, exposure of an ester to hydrolysis conditions results in a decrease in the starting materials (*i.e.*, ester and water) and an increase in the products (*i.e.*, alcohol and carboxylic acid or carboxylate salt).

8. As would have been readily understood by one of skill in the art, tannic acid comprises at least one carboxylic ester formed from 3,4,5-trihydroxybenzoic acid and a sugar (*e.g.*, glucose). Applying the reaction scheme referenced above to tannic acid, one of skill in the art would understand that tannic acid would have been hydrolyzed to produce 3,4,5-trihydroxybenzoic acid and a sugar derivative:





9. As a result, the free gallic acid (3,4,5-trihydroxybenzoic acid) content in tannic acid would have increased under hydrolysis conditions. The knowledge that hydrolysis would in fact increase the amount of free gallic acid within tannic acid actually teaches away from selecting tannic acids having less than about 1% gallic acid.
10. I have reviewed the Office Action mailed October 4, 2006, and the references cited therein. In particular, I have read and understood U.S. Patent No. 5,738,688 to De Lathauwer (hereinafter "De Lathauwer"), U.S. Patent No. 4,482,646 to Gamblin (hereinafter "Gamblin"), U.S. Patent No. 4,094,701 to Fekete (hereinafter "Fekete"), U.S. Patent No. 5,520,962 to Jones, Jr. (hereinafter "Jones"), and U.S. Patent No. 5,403,362 to Gurley (hereinafter "Gurley").
11. Based on my review of these references, it is my opinion that the claimed invention would have been unexpected and, therefore, would not have been obvious to one of ordinary skill in the art of carpet manufacture and carpet treatment at least because none of the cited references discloses a method of treatment that achieves the superior results of the claimed methods.
12. Based on my review of De Lathauwer, it is my opinion that the claimed invention would not have been obvious to one of ordinary skill in the art of carpet manufacture. While De Lathauwer states that any commercial tannic acid can be used, De Lathauwer does not suggest the selection of a tannic acid having a gallic acid content of less than about 1.0 part



by weight to practice its methods. In fact, De Lathauwer is silent as to the free gallic acid content of the tannic acid.

13. Further, based on my review of De Lathauwer, I conclude that one of ordinary skill in the art of carpet manufacture would not have been motivated by De Lathauwer to modify the gallic acid content to within the claimed amount. Because De Lathauwer provides no teaching as to the gallic acid content of the tannic acid, one having ordinary skill in the art of carpet manufacture would not have understood that stain resistance could have been improved by selecting a tannic acid having a certain gallic acid content, much less a gallic acid content of less than about 1.0 part by weight.
14. Based on the foregoing, I conclude that those of skill in the art would not have understood from De Lathauwer, or any other cited reference, that there was a relationship whatsoever between gallic acid content in tannic acid and improved stain resistance.
15. In contrast to the methods of De Lathauwer, the claimed invention relates to improved stain resistance observed when a treatment comprising tannic acid having less than 1 part by weight gallic acid is selected. Specifically, the compositions and methods of the present invention provide improved resistance to "browning," which can be caused by contact of fiber, yarn, or carpet with relatively high pH cleaning compositions, which are often used during routine maintenance of fiber, yarn, or carpet.
16. In order to demonstrate the superiority of the compositions and methods in the present application, the tests disclosed in the application were performed under my supervision. The tendency of fiber, yarn, or carpet to "brown" when contacted with high pH cleaning compositions was evaluated by measuring the color difference in a fiber, yarn, or carpet before and after application of a 10% by weight sodium hydroxide solution. The color difference was evaluated by using a Macbeth contact spectrophotometer model 20/20 ("Macbeth") and by using a visual gray scale rating system as described in ISO 105-A02 ("ISO 105-A02").

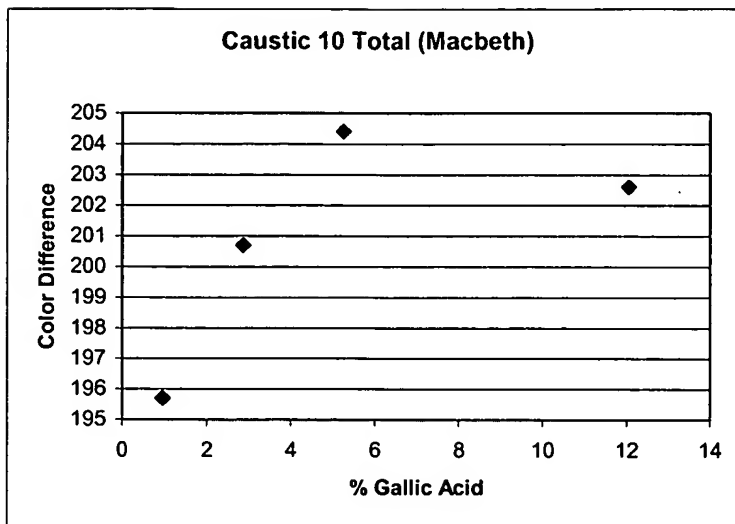


17. As described at page 31 of the specification, four tannic acids having differing gallic acid contents were evaluated. The “Caustic 10” test, using both the “Macbeth” and the “ISO 105-A02” measurement methods, was used to evaluate samples of treated fiber, yarn, or carpet, as set forth in Table 4 (page 38), Table 6 (page 41), Table 8 (page 44), and Table 10 (page 47) of the specification, as filed. Exemplary results are summarized below:

<b>Tannic Acid</b>	<b>% Gallic</b>	<b>Caustic 10 (Macbeth)</b>	<b>Caustic 10 (ISO 105-A02)</b>
<b>ASP</b>	0.96	195.7	17.5
<b>3SP</b>	2.87	200.7	16.5
<b>CLM</b>	5.26	204.4	16.5
<b>BAYGARD® CL Liquid</b>	12.05	202.6	16.5

18. As described at page 31 of the specification, tannic acids having differing gallic acid contents were evaluated in a “Caustic 10” test, using the “Macbeth” measurement method. A material treated with a tannic acid having 0.96% gallic acid provided a score of 195.7, while materials treated with a tannic acid having gallic acid contents of 2.87%, 5.26%, and 12.05% provided scores of 200.7, 204.4, and 202.6, respectively.

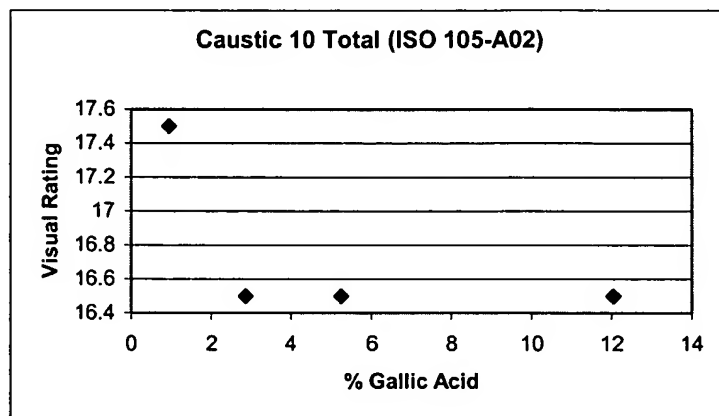




19. A lower “Macbeth” measurement for the Caustic 10 test denotes that the samples have a smaller change in coloration (*i.e.*, less “browning”) due to exposure to a 10% by weight sodium hydroxide solution; this indicates superior stain resistance. Based upon these measurements as well as my visual comparison of a material treated with tannic acid having less than about 1% gallic acid with a material treated with tannic acid having greater than about 1% gallic acid, I conclude that there is a distinct improvement in stain resistance to “browning” for a material treated with tannic acid having less than about 1 part by weight gallic acid.
20. Likewise, as also described in the specification, tannic acids having differing gallic acid contents were evaluated in a “Caustic 10” test, using the “ISO 105-A02” measurement method. A higher “ISO 105-A02” measurement for the Caustic 10 test denotes that the samples appear less “browened” after exposure to a 10% by weight sodium hydroxide solution; this indicates superior stain resistance. A material treated with a tannic acid having 0.96% gallic acid provided a score of 17.5, while materials treated with a tannic acid having gallic acid contents of 2.87%, 5.26%, and 12.05% provided scores of 16.5, 16.5, and 16.5, respectively.



21. The visual rating (“ISO 105-A02”) for samples contacted with a 10% by weight sodium hydroxide solution is unexpectedly higher for samples treated with tannic acid having less than about 1% gallic acid, as shown in the graph below:



22. Based on the resulting data, I conclude that the disclosed compositions and methods provide unexpectedly superior results when tannic acid having less than 1 part by weight gallic acid is selected as compared to compositions and methods of the prior art.
23. Based on all of the foregoing and on my knowledge of what those of skill in carpet manufacturing would have known, I conclude that those of skill in the art of carpet manufacture at the time the invention was made would not have reasonably expected that stain resistance to “browning” could have been improved by selecting and using a tannic acid having a gallic acid content of less than about 1.0 part by weight.
24. Thus, the substantially superior resistance to browning observed when using the claimed compositions to treat, *e.g.*, fiber, yarn or carpet indicates that the claimed compositions are not obvious over De Lathauwer, Gamblin, Fekete, Jones, Gurley, or any combination thereof.
25. Additionally, unexpectedly superior stain resistance (for both total stain and for caustic) is achieved when applying a two-part aqueous treatment comprising a first aqueous treating composition comprising tannic acid and a separate second topical treating composition comprising a fluorochemical.



26. The results from the Examples reveal that use of the claimed compositions provide a lower Caustic 10% (shown in Table as “Caustic”) measurement (a lower number translates to decreased “browning”) as well as a lower Total Stain (shown in Table as “Total”) measurement (a lower number translates to improved resistance to staining in general). A summary of data from Tables 3-10 (*see* pages 37-47 of the specification as filed) is tabulated in the Table below:

Table

Sample Conditions		ASP (0.96%) <sup>1</sup> Table 4, p.38		3SP (2.87%) <sup>2</sup> Table 6, p.41		CLM (5.26%) <sup>3</sup> Table 8, p.44		BayGard CL (12.05%) <sup>4</sup> Table 10, p.47	
		Caustic	Total	Caustic	Total	Caustic	Total	Caustic	Total
<b>A</b>	Beck Exhaust (De Lathauwer)	16.2	104.9	14.2	76	18.3	104.8	21.1	80.5
<b>B</b>	Beck Exhaust (De Lathauwer) plus fluorochemical in bath	26.6	133.1	27.7	121.8	24.8	83.2	23	84.4
<b>C</b>	Beck Exhaust (conventional SR)	16.5	51.2	17	57.1	17.1	50.15	15.1	47.4
<b>D</b>	Beck Exhaust (conventional SR) plus fluorochemical in bath	15.7	56.3	14.8	47.4	16	56.3	13.4	47.4
<b>E</b>	Continuous (De Lathauwer)	16.4	108.4	15.5	107	20.9	94.5	22.4	104.8
<b>F</b>	Continuous (De Lathauwer) plus Alum	16.7	80.9	19.9	96.1	13.3	66.7	10.1	67.4
<b>G</b>	Continuous (De Lathauwer) plus fluorochemical in bath	16.2	90.1	16.4	87.5	16	71.3	21.9	84.9
<b>H</b>	Continuous (De Lathauwer) plus fluorochemical in bath plus Alum	15.3	78.5	14.4	82.4	11.7	67.8	11.5	67.1
<b>I</b>	Continuous (conventional SR)	18.9	93.2	13.1	82.4	15.5	89.9	17.5	99.1
<b>J</b>	Continuous (conventional SR) plus fluorochemical in bath	21.7	52.6	21.7	55.6	25.6	74.15	25.5	71.3
<b>K</b>	Invention (Beck Exhaust)	9.4	31.3	13.3	45.5	13.3	46.2	16	47.8
<b>L</b>	Invention (Continuous)	6.1	35.9	12.7	56.05	11.9	58.1	5.1	50.4

<sup>1</sup> Conditions for Samples A-L for ASP treated samples/controls are taken from Table 3, page 37.

<sup>2</sup> Conditions for Samples A-L for 3SP treated samples/controls are taken from Table 5, page 40.

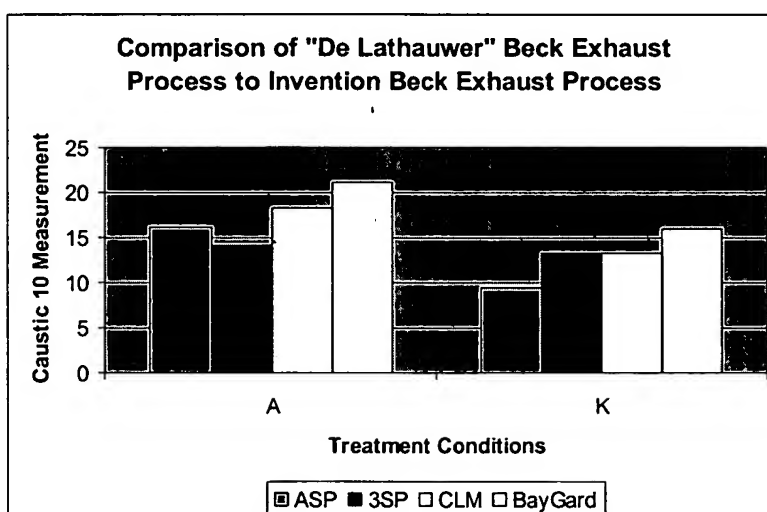
<sup>3</sup> Conditions for Samples A-L for CLM treated samples/controls are taken from Table 7, page 43.

<sup>4</sup> Conditions for Samples A-L for BayGard CL treated samples/controls are taken from Table 9, page 46.



27. For example, comparison of a Beck Exhaust process with treatment conditions analogous to those used in De Lathauwer (Table, entry A and Graph I, columns A) with a Beck Exhaust process with treatment conditions as claimed in the present invention (Table, entry K and Graph I, columns K) demonstrates that the claimed compositions, when compared to conventional compositions (*e.g.*, De Lathauwer) provides a substantially superior caustic 10 measurement (here, as much as about, *e.g.*, 42% lower).

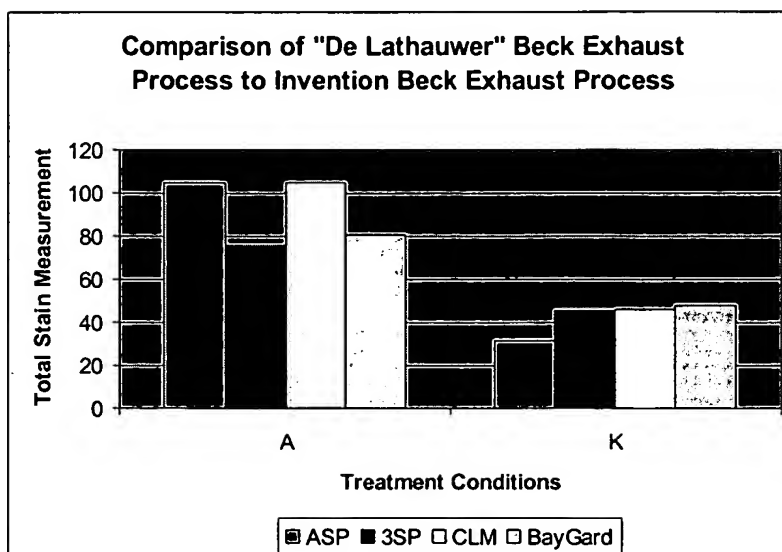
**Graph I**



28. Likewise, comparison of a Beck Exhaust process with treatment conditions analogous to those used in De Lathauwer (Table, entry A and Graph II, columns A) with a Beck Exhaust process with treatment conditions as claimed in the present invention (Table, entry K and Graph II, columns K) demonstrates that the claimed compositions, when compared to conventional compositions (*e.g.*, De Lathauwer) provides a substantially superior total stain measurement (here, as much as about, *e.g.*, 70% lower).



Graph II

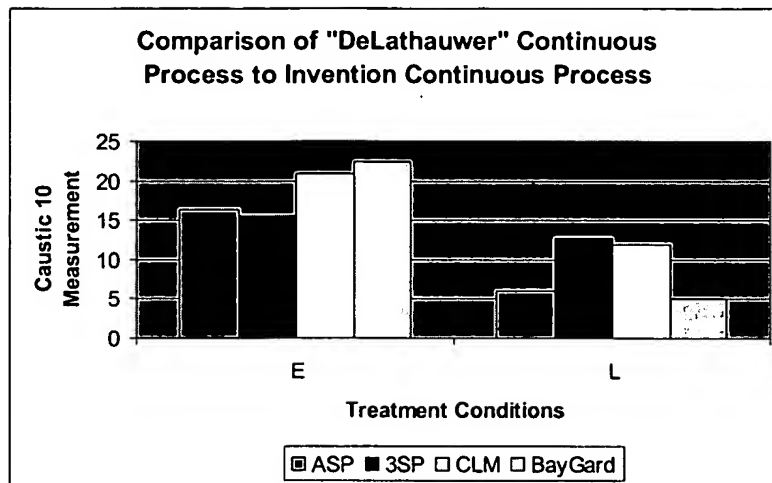


29. Such improvement is also evident for the claimed methods in a continuous process.

Comparison of a continuous process with treatment conditions analogous to those used in De Lathauwer (Table, entry E and Graph III, columns E) with a continuous process with treatment conditions as claimed in the present invention (Table, entry L and Graph III, columns L) demonstrates that the claimed method, when compared to conventional methods (*e.g.*, methods analogous to De Lathauwer) provides a substantially superior caustic 10 measurement (here, as much as about, *e.g.*, 63% lower).

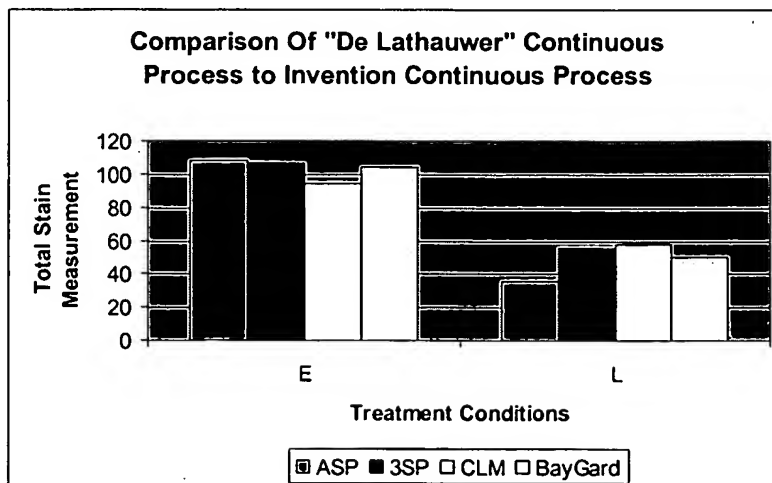


Graph III




30. Again, this improvement is also evident for the claimed compositions for total stain measurement in a continuous process. Comparison of a continuous process with treatment conditions analogous to those used in De Lathauwer (Table, entry E and Graph IV, columns E) with a continuous process with treatment conditions as claimed in the present invention (Table, entry L and Graph IV, columns L) demonstrates that the claimed compositions, when compared to conventional compositions (*e.g.*, De Lathauwer) provides a substantially superior total stain measurement (here, as much as about, *e.g.*, 67% lower).

Graph IV





31. No such improved stain resistance is disclosed or suggested anywhere in the cited references.
32. I declare that all statements made herein of my own knowledge and belief are true and that all statements made on information and belief are believed to be true, and further, that the statements are made with the knowledge that willful false statements are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

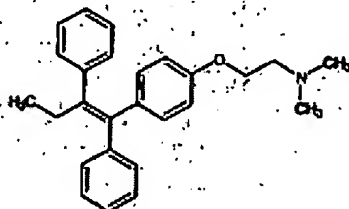
  
\_\_\_\_\_  
Dennis J. Jones, Jr.  
Dated: 2/21/07



Tannic Acid

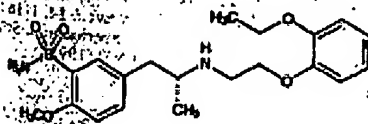
9141

3-oxo-2-phenyl-1,2-diphenylbut-1-ene.  $C_{22}H_{19}NO$ ; mol wt 371.51. C 84.06%, H 7.87%, N 3.77%, O 4.31%. Non-steroidal estrogen antagonist. Prep: BR 637389 (1964 to ICI). Identification and separation of isomers: G. R. Bedford, D. N. Richardson, *Nature* 212, 733 (1966); BR 678807; M. J. K. Harper et al. US 4536516 (1966, 1983 both to ICI). Stereospecific synthesis: R. B. Miller, M. I. Al-Hassan, *J. Org. Chem.* 50, 2121 (1985). Review of chemistry and pharmacology: B. J. A. Plur, V. C. Jordan, *Pharmacol. Ther.* 25, 127-205 (1984). Reviews of clinical experience in treatment and prevention of breast cancer: I. A. Jolyssimi et al., *J. Clin. Oncol.* 13, 513-529 (1995); C. K. Osborne, *N. Engl. J. Med.* 339, 1609-1618 (1998).

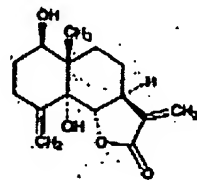


Crystals from petr ether, mp 96-98°. Citrate. [54965-24-1] ICI-46474; Keston; Nolvadex; Tamoxifen; Zanolde; Zanolone;  $C_{22}H_{19}NO \cdot C_6H_5O_7$ ; mol wt 563.64. Fine, white, odorless crystalline powder, mp 140-142°. Slightly sol in water; sol in ethanol, methanol, acetone. Hygroscopic at high relative humidities. Sensitive to uv light. LD<sub>50</sub> is 1000 mg/kg (rat, ip); 200, 600 ip; 62.5, 62.5 iv; 3000-6000, 1000-2500 orally (rat, ip; Jordan). (Z)-Folch. [13002-65-8] mp 72-74° from methanol. (Z)-Form citrate. ICI-47699, mp 126-128°. Note: Tamoxifen has been listed as a known human carcinogen: *High Report on Carcinogens* (PB2000-107509, 2000) p 11-11.

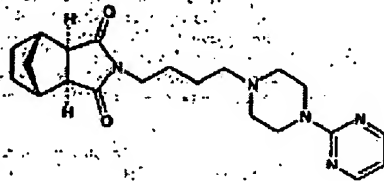
THERAP CAT: Antiestrogen; antineoplastic (hormonal). 9133. Tamoxifen. [106133-20-4] 5-[(2R)-2-[(2-ethoxyphenyl)ethyl]phenyl]-2-methoxybenzoic acid;  $C_{26}H_{24}O_3$ ; mol wt 408.52. C 80.80%, H 6.91%, N 6.85%, O 19.89%, S 7.85%. Specific  $\alpha_1$ -adrenoceptor antagonist. Prep: K. Lind et al., EP 34432; *idem*, US 4703063 (1991, 1997 both to Yamamoto). Comparative pharmacology of tamoxifen and racemate: K. Honda et al., *Arch. Pharmacol.* 336, 233 (1997). HPLC determin in plasma: Y. Sasaki et al., *J. Chromatogr.* 533, 291 (1990). Clinical trials in benign prostatic hyperplasia: K. Kawabe et al., *J. Urol.* 144, 903 (1990); Y. Arai et al., *Brit. J. Urol.* 76, 325 (1995).



Prophylaxis. [106463-17-6] LY-253351; YM-12617-1; 74-67; 74-67; Harnal; Omnic; Proflid.  $C_{22}H_{21}N_3O_3 \cdot HCl$ ; mol wt 425.43. mp 228-230°.  $[\alpha]_D^{25} -4.0^\circ$  ( $c = 0.35$  in methanol). Treatment of benign prostatic hyperplasia. 9134. Harnal. [1401-54-3] [3aS-(3aR,5aR,6aR,9aR)-9a,10a-dihydroxy-5a-methyl-3,9-bis(methoxy)-1,2,3,4-tetrahydronaphthalen-2(3H)-one; 1,5a-dihydroxy-6a,7a-dihydro-2(3H)-one.  $C_{17}H_{23}O_5$ ; mol wt 264.32. mp 133-135°. 100% from seed, herb, and other parts of *Hamamelis* L., *Compositae*: Hamolle, *J. Pharm. Med.* (1845); Jaretsky, Kihne, *Arch. Pharm.* 271, 353 (1933); Suchy, *Coll. Czech. Chem. Commun.* 27, 1058 (1962). Structure and absolute config: Samck et al., *ibid.* 33, 1971 (1973).



Crystals, mp 205°.  $[\alpha]_D^{25} +179.5^\circ$  ( $c = 2.3$  in ethanol). 9140. Tandespiro. [87760-53-0] (3aR,4R,7R,8aR)-Hexahydro-2-[4-(4-(2-pyrimidinyl)-1-piperazinyl)butyl]-4,7-methano-1H-indole-1,3(2H)-dione; (1R\*,2S\*,3R\*,4S\*)-4-[4-(2-pyrimidinyl)-1-piperazinyl]butyl]-2,3-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid;  $C_{21}H_{24}N_4O_3$ ; mol wt 383.49. C 63.77%, H 7.62%, N 18.26%, O 8.34%. Serotonin (5-HT<sub>1A</sub>) receptor agonist. Prep: K. Ishizumi et al., EP 82402; *idem*, US 4507303 (1983, 1985 both to Sumitomo); Ishizumi et al., *Chem. Pharm. Bull.* 39, 2288 (1991). Behavioral pharmacology: C. A. Schmechel et al., *Drug Ab. Depend.* 32, 195 (1993). Clinical efficacy in treatment of bulimia: H. Tamai et al., *Int. J. Obesity* 14, 289 (1990). Clinical evaluation of potential adverse effects: M. Suzuki et al., *Japan. J. Psychopharmacol.* 13, 213 (1993); of abuse liability: S. M. Evans et al., *J. Pharmacol. Exp. Ther.* 271, 683 (1994). Review of pharmacology: P. A. Seymour et al., *Prog. Clin. Biol. Res.* 361, 433-460 (1990).



Crystals from toluene-hexane, mp 112-113°. Citrate. [112457-95-1] SM-3997; Sertal.  $C_{17}H_{19}N_3O_2 \cdot C_6H_5O_7$ ; mol wt 573.61. mp 169.3-170°. Hydrochloride,  $C_{17}H_{19}N_3O_2 \cdot HCl$ . Crystals from isopropanol, mp 227-229°. THERAP CAT: Anxiolytic; antidepressant.

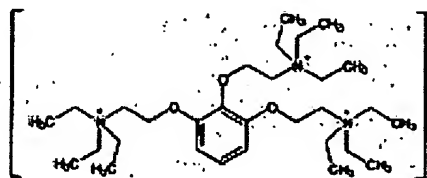
9141. Tannic Acid; Tannin; gallocatechin; gallocatechin acid. Incorrectly "gallic acid". Tannic acid of commerce usually contains about 10% H<sub>2</sub>O. Occurs in the bark and fruit of many plants, notably in the bark of the oak species, in sumac and myrobalan. It is produced from Turkish or Chinese galls, the former contg 50-60%, the latter about 70%. The chemistry of the tannins is most complex and non-uniform. Tannins may be divided into 2 groups: (a) derivatives of flavanols, so-called condensed tannins and (b) hydrolyzable tannins (the more important group) which are esters of a sugar, usually glucose, with one or more trihydroxybenzoic acids. The structure given here is that of a tannin named corilagin; Schmidt et al., *Ann.* 587, 67 (1954). The empirical formula of corilagin is  $C_{47}H_{32}O_{11}$ . For the commercial tannic acid, whose specifications follow, the empirical formula is usually given as  $C_{27}H_{34}O_{14}$ . Toxicity study: Robinson, Grinstead, *J. Pharmacol. Exp. Ther.* 77, 63 (1943). Comprehensive reviews: M. Nierenstein, *The Natural Organic Tannins* (London, 1934); O. Th. Schmidt, "Gallocatechin" in *Fortschr. Chem. Org. Naturst.* 13, 70-136 (1956); Symposium on the Chemistry of Vegetable Tannins (Soc. Leather Trades Chemists, Croydon 1956).



4364

## Gallamine Triethiodide

**4364. Gallamine Triethiodide.** [63-29-2] 2,2',2''-[1,2,3-Benzene-tris(oxy)]tris(*N,N,N*-triethylthammonium) triiodide; [*p*-phenyltris(oxyethylene)]tris(triethylthammonium triiodide); 1,2,3-tris(2-triethylthammonium ethoxy)benzene triiodide; 1,2,3-tris(2-diethylthammonioethoxy)benzene tris(ethyl iodide); tri-( $\beta$ -diethylthammonioethoxy)-1,2,3-benzene triiodoethylate; pyrogallol 1,2,3-(diethylthammonioethyl ether) tris(ethyl iodide); benzene triiodide; RP-3697; P-2559; Relaxin; Flaxedil.  $C_{36}H_{60}I_3N_3O_3$ ; mol wt 891.53. C 40.42%, H 6.78%, I 42.70%, N 4.71%, O 5.38%. Characterizing properties: D. Bovey et al., *Compt. Rend.* 225, 74 (1947); F. Depierre, *ibid.* 956. Preps: E. Fourniau, US 2544876 (1951 to Rhone-Poulenc). Comparative clinical pharmacokinetics: W. Buzzell, S. Agostino, *Anaesthetist* 27, 313 (1978). Mode of action: D. Colquhoun, R. E. Sheridan, *Brit. J. Pharmacol.* 66, 78 (1979); *idem*, *Proc. Roy. Soc. London, Ser. B* 211, 181 (1981). Effects in mammals and amphibian nerve fibers: K. J. Smith, C. L. Schoof, *Science* 212, 1170 (1981).

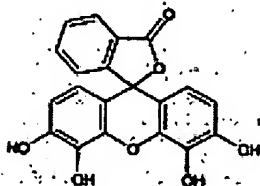


White cryst from acetone/water, mp 152-153° (indefinite). Freely sol in water, alc, dil acetone; sparingly sol in anhyd acetone, ether, benzene, chloroform.

**THERAP CAT:** Neuromuscular blocking agent.

**THERAP CAT (VET):** Neuromuscular blocking agent.

**4365. Gallin.** [2103-64-2] 3',4',5',6'-Tetrahydroxy-spiro(isobenzofuran-1(3H),9'(9H)xanthen)-3-one; 3',4',5',6'-tetrahydroxyfluoran; 3',4',5',6'-tetrahydroxyspiro[phenanthrene-1,9'-xanthen]-3-one; pyrogallolphenalein; C.I. 45445; mordant violet 25.  $C_{20}H_{12}O_7$ ; mol wt 364.30. C 65.94%, H 3.32%, O 30.74%. Obtained by heating 1 part phthalic anhydride with 2 parts of pyrogallol or gallic acid: Beyer, *Ber.* 4, 457 (1871); Buchka, *Ann.* 209, 261 (1881). Use as a biological stain: R. D. Little et al., *State Technol.* 43, 339 (1974); R. Welsh, *ibid.* 52, 261 (1977). See also H. J. Conn's *Biol. Stains*, R. D. Little, Ed. (Williams & Wilkins, Baltimore, 9th ed., 1977) p 351.



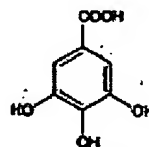
Brownish-red powder or crystals with 14 H<sub>2</sub>O, or red crystals with greenish-yellow color when anhydr. Loses the water of cryst at about 180° and blackens above this temp. Does not melt even at 300°. pH 3.8 brownish-yellow; pH 6.6 rose-red. Almost insol in water, benzene, chloroform. Slightly sol in ether; sol in alc, acetone, alkalies.

Dibodum salt. Alizarin violet.  $C_{20}H_{12}O_7Na_2O_4$ . pH 10.6 rose; pH 13.0 violet.

**USE:** Clinical reagent (phosphates in urine). Monophosphates give a yellow, dibasic a red, tribasic a violet color. Used in soln of 0.5 g in 100 ml 50% alc; 2-3 drops for 100 ml liq. As sensitive indicator for acids, alkali hydroxides, NH<sub>3</sub>, but not for carbonates. Biological stain.

**4366. Gallic Acid.** [149-91-7] 3,4,5-Trihydroxybenzoic acid.  $C_7H_6O_5$ ; mol wt 170.12. C 49.42%, H 3.55%, O 47.02%. Obtained by alkaline or acid hydrolysis of the tannins from gall; also by enzymatic hydrolysis using spent broths from *Pen-*

*icillium glaucum* or *Aspergillus niger* which contain: Iwama, A. G. Peikin, O. Gannell, *J. Chem. Soc.* 69, 1303 (1896); Hahn, *Huang Hai* No. 7, 51 (1946), *C.A.* 42, 3901i (1948); Cochran, *Econ. Bot.* 2, 145 (1948); Toth, Henster, *Acta Chim. Acad. Sci. Hung.* 2, 209 (1952). Preps from tannin containing materials: Krueger et al., US 2723992 (1955 to Mallinckrodt). Synthesis from aliphatic materials: Shipchandlor et al., *J. Chem. Soc. Perkin Trans. I* 1973, 1400. Biosynthesis: Haslam et al., *J. Chem. Soc.* 1961, 1854. Study of polymorphic forms: E. Lindqvist, *Mikrochimie* 27, 21 (1939). Toxicity studies: J. W. Doherty et al., *Am. J. Vet. Res.* 23, 1264 (1962).



Needles from abs methanol or chloroform, formerly reported as dec 235-240° (Peklin, Gannell). Sublimes at 210° giving a stable form with mp 258-265° (dec) and an unstable form mp 225-230° (Lindqvist). One gram dissolves in 87 ml water, 3 ml boiling water, 6 ml alcohol, 100 ml ether, 10 ml glycerol, 5 ml acetone. Practically insol in benzene, chloroform, pet ether. Protect from light. LD<sub>50</sub> in rabbits (g/kg): 5.0 orally (Dollahite).

**Methyl ester.** [99-24-1] Methyl gallate; gallatin.  $C_8H_8O_5$ . Monoclinic prisms from methanol, often hydrated or solvated. When dry, mp 202°. Sol in hot water, alcohol, methanol, ether.

**Propyl ester, see Propyl Gallate**

**USE:** Mannif-gallic acid esters, pyrogallol; tints; airphoto-graphic developer; in tanning; in dyeing; in testing for free mineral acids, dihydroxyacetone and alkaloids. Empers as mordants.

**THERAP CAT:** Formerly as astringent, astringe.

**THERAP CAT (VET):** Has been used as intestinal astringent.

**4367. Gallium.** [7440-55-3] Ga; at. wt 69.723; at. no. 31; valences 3, 2, 1. (Group IIIA(13). Natural isotopes: 69 (60.2%); 71 (39.8%); artificial radioactive isotopes: 63-68; 70; 72-76. Best source is the mineral germanite, a copper sulfide ore; occurs in very small quantities in zinc blende, in aluminum ores, found in ores of iron, chromium, manganese; constitutes 5 x 10<sup>-4</sup>% of the crust of the earth. Discovered by L. Boissaudran, *Compt. Rend.* 81, 493, 1100 (1875); 82, 163, 1036 (1876); isolated pure by L. Boissaudran and E. Jungfleisch, *Bull. Soc. Chim.* (2) 31, 50 (1879). Isob from rhodium-rich copper schist: Felt, *Angew. Chem.* 46, 216 (1933). From bauxite: *Chem. Eng. News* 34, 4300 (1956). Purification by zone melting: *Chem. Ztg.* 80, 787 (1956). Alternate methods of purification: Gombur, US 2928731; Merkel, US 2927853 (both 1960 to Siemens-Schuckert). Spectra: L. Boissaudran et al., cited in *Mellor's* vol. 5, 378 (1929). Reviews: Wagner, Glitzen, *J. Chem. Ed.* 29, 162 (1952); Greenwood, *Inorg. Chem. Radiochem.* 5:91-134 (1963); Wade, Banister, *Comprehensive Inorganic Chemistry* vol. 1, J. C. Bailar, Jr. et al., Eds. (Pergamon Press, Oxford, 1973) pp 997-1000, 1069-1117; P. de la Breuille in *Kirk-Othmer Encyclopedia of Chemical Technology* vol. 11 (Wiley-Interscience, New York, 3rd ed., 1980) pp 604-620.

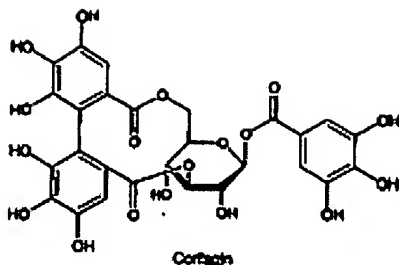
Grayish-metal; possesses a greenish-blue reflection; tin- or silver-like when molten; has a crystalline orthorhombic texture. mp 29.78°. bp approx 2400°. Cochran, Foster, *J. Electrochem. Soc.* 109, 144 (1962). Shows a tendency to reoxidize in super-cooled state. Contracts on melting:  $d^{25}_4$  (solid) 5.9037;  $d^{25}_4$  (liq) 6.0947; Richards, Boyer, *J. Am. Chem. Soc.* 43, 274 (1921). Heat capacity: 0.09 cal/g°C (0-24°; solid). Latent heat of fusion 19.16 cal/g. Stable in dry air; tarnishes in moist air or oxygen. Reacts with acids with evolution of hydrogen; attacked by cold concd hydrochloric acid; rendered passive by hot nitric acid; readily attacked by halogens.

**Sesquioxide.**  $Ga_2O_3$ . Obtained by thermal decomn of the salts; exists in five crystalline modifications.  $\beta$ -Form is most stable, mp 1740 $\pm$ 20°.  $d$  5.94. On heating with magnesium is violently reduced to the metallic state.



9142

Tannosform



Yellowish-white to light brown, amorphous, bulky powder or flakes, or spongy masses; faint characteristic odor; astringent taste. Gradually darkens on exposure to air and light; at 210-215° dec mostly into pyrogallol and CO<sub>2</sub>. Gives insol ppt with albumin, starch, gelatin, most alkaloidal and metallic salts; produces a bluish-black color or precip with ferric salts. One gram dissolves in 0.33 ml water, 1 ml warm glycerol; very sol in alc, acetone. Practically insol in benzene, chloroform, ether, per ether, carbon disulfide, carbon tetrachloride. Keep well closed and protected from light. LD<sub>50</sub> orally in mice: 6.0 g/kg (Robinson, Oranston).

USE: Mordant in dyeing; mordant ink; sizing paper and silk; printing fabrics; with gelatin and albumin for manuf of imitation bone and tortoise shell; tanning; clarifying beer or wine; in photography; as coagulant in rubber tannin; mordant gallic acid and pyrogallol; as reagent in analytical chemistry.

THERAP CAT: Astringent.

THERAP CAT (VET): Astringent, hemostatic, in solutions for burns. Has been used internally as an astringent and as a heavy metal antidote.

9142. Tannosform. [9010-29-1] Methylcondannin; trimethylformaldehyde; Helgouss. Prep'd by condensing one mole formaldehyde with two moles tannin. Chemistries, Pharm. Zentrbl. 63, 273 (1927); Schweitzer, Pharm. Ztg. 74, 1334 (1929). Reddish, odorless, tasteless, bulky powder, mp -230° with decomp. Practically insol in water; sol in alcohol, alkaline fluids.

THERAP CAT: Astringent.

THERAP CAT (VET): Externally as astringent, antiseptic (skin lesions and otitis). Has been used internally for diarrhea.

9143. Tantalum. [7440-25-7] Ta; at. wt 180.9479; at. no. 73; valence 5, also 4, 3, 2. Group VB(5). Two naturally occurring isotopes: 181 (99.9877%); 180 (0.0123%). T<sub>m</sub> > 10<sup>3</sup> years; artificial radioactive isotopes: 172-179; 182-186. Occurs almost invariably with niobium; less abundant than niobium. Found in the minerals columbite, q.v., tantalite [(Fe,Mn)(Ta,Nb),O<sub>6</sub>] and niobite [(Na,Ca),Ta<sub>2</sub>O<sub>6</sub>(OH,F)]. Discovered by Ekeberg in 1802; first obtained pure by Böhman. Z. Elektrochem. 11, 45 (1905). Preps: Schoeller, Powell, J. Chem. Soc. 419, 1927 (1921). Reviews of tantalum and its compounds: O. L. Miller, *Tantalum and Niobium* (Academic Press, New York, 1959) 767 pp; Brown, "The Chemistry of Niobium and Tantalum" in *Comprehensive Inorganic Chemistry* vol. 3, J. C. Bailar, Jr. et al., Eds. (Pergamon Press, Oxford, 1973) pp 553-622.

Gray, very hard, malleable, ductile metal; can readily be drawn in fine wires, mp 2996°, bp 5429°, d 16.69. Spec heat (0°): 0.036 cal/g°C. Electrical resistivity (18°): 12.4 μohm-cm. Insol in water. Very resistant to chemical attack; not attacked by acids other than hydrofluoric; not attacked by alkalis; slowly attacked by fused alkalis. Reacts with fluorine, chlorine, and oxygen only on heating. At high temps absorbs several hundred times its volume of hydrogen; combines with nitrogen, with carbon.

Caution: Potential symptoms of overexposure to metal and oxide dust are irritation of eyes and skin. See NIOSH-Pocket Guide to Chemical Hazards (DHHS/NIOSH 97-140, 1997) p 294.

USE: In pen points; analytical weights; apparatus and instruments for chemical, surgical, and dental use instead of platinum.

in tantalum capacitors (a type of electrolytic condenser, not marked "Tantadytic").

9144. Tantalum Pentachloride. [7721-01-9] Cl<sub>5</sub>Ta; mol wt 358.21. Cl 49.49%, Ta 50.51%. TaCl<sub>5</sub>. Prep'd from tantalum pentachloride by the halide exchange method according to its equation TaCl<sub>5</sub> + 5HF → TaF<sub>5</sub> + 5HCl. Russ. Zashch. Ser. 4, 492 (1909); Ruff, Schiller, Z. Anorg. Allgem. Chem. 72, 35 (1911); Krasnik in *Handbook of Preparative Inorganic Chemistry* vol. 1, G. Brauer, Ed. (Academic Press, New York, 2nd ed, 1963) pp 255-256. Preps from the elements: Fairbrother, Friith, J. Chem. Soc. 1951, 3051. Review of transition metal pentachlorides: Peacock, *Advan. Fluoride Chem.* 7, 113-116 (1973).

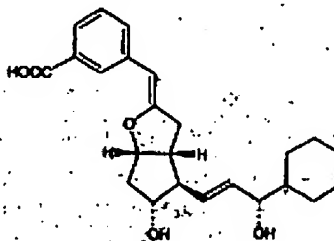
Deliquescent, strongly refractive prisms. d<sub>4</sub> 4.74, mp 96.2°. Also reported as 93.1°. Fairbrother, Friith, loc. cit. bp 239.2°. Sol in water and ether with formation of oxyfluoro complexes. Also sol in concentrated nitric acid, more sol in fuming nitric acid. Sparingly sol in hot carbon disulfide and hot carbon tetrachloride. Etches glass slowly.

USE: Friedel-Crafts catalyst.

9146. Tantalum Pentoxide. [1314-61-0] Ta<sub>2</sub>O<sub>5</sub>; mol wt 441.89. O 18.10%, Ta 81.90%. Ta<sub>2</sub>O<sub>5</sub>. Acute toxicity: K. W. Cochran et al., *Arch. Ind. Hyg. Occup. Med.* 1, 637 (1950).

White, microcrystalline, infusible powder. Insol in water, alcohol, mineral acids. Sol in HF. Dec by fusing with KHSO<sub>4</sub> or KOH, forming potassium tantalate with the latter. LD<sub>50</sub> only in rats: 8000 mg/kg (Cochran).

9147. Tiroprostene. [108945-35-3] 3-(2-((3,4,4,4-tetrafluoro-5-hydroxy-2H-cyclopenta[b]furan-2-ylidene)methyl)phenyl)-5-hydroxy-2H-cyclopenta[b]furan-2-ylidene)methyl)-4-((1E,3E)-3-cyclohexyl-3-hydroxy-1-propenyl)benzoic acid; α-((2Z,3R,4R,5R,6aS)-4-((1E,3E)-3-cyclohexyl-3-hydroxypropenyl)hexahydro-5-hydroxy-2H-cyclopenta[b]furan-2-ylidene)-methyl)-5-oxo-1,1,1,5-tetrahydro-2,3,4-epoxy-1,1,5-dihydroxy-15-cyclohexyl-16,17,18,19,20-pentamethylprosta-5,13-dienoic acid, C<sub>36</sub>H<sub>42</sub>O<sub>7</sub>; mol wt 598.49. C 72.34%, H 7.59%, O 20.06%. Prostacyclin analog; platelet aggregation inhibitor. Preps: U. Selpp et al., EP 45842; *idem*, US 4372971 (1982, 1983) to Grunenthal; L. Flohé et al., *Arzneimittel-Forsch.* 33, 1240 (1983). As adjuvant to thrombolytic therapy in acute myocardial infarction: F. W. Eiki et al., *Eur. Heart J.* 14, 1118 (1993). Review of pharmacology and clinical experience: J. Schneider et al., *Cardiovasc. Drug Rev.* 11, 479-500 (1993).



Sodium salt. [87440-45-7] CG-4203; Rhoocyclan. C<sub>36</sub>H<sub>41</sub>NaO<sub>7</sub>; mol wt 420.47. [α]<sub>D</sub><sup>25</sup> +249° (c = 0.68 in methanol). LD<sub>50</sub> in mice, rats (mg/kg): 164, 20 i.v. (Schneider).

THERAP CAT: Antithrombotic.



**tall oil.** (tallol; liquid rosin). A mixture of rosin acids, fatty acids, and other materials obtained by acid treatment of the alkaline liquors from the digesting (pulp) of pine wood; flash p 360F (182C). Combustible.

**Derivation:** The spent black liquor from the pulping process is concentrated until the sodium salts (soaps) of the various acids separate out and are skimmed off. These are acidified by sulfuric acid. Composition and properties vary widely, but average 35-40% rosin acids, 50-60% fatty acids.

**Grade:** Crude, refined.

**Use:** Paint vehicles, source of rosin, alkyd resins, soaps, cutting oils and emulsifiers, driers, flotation agents, oil-well drilling muds, core oils, lubricants and greases, asphalt derivatives, rubber reclaiming, synthesis of cortisone and sex hormones, chemical intermediates.

**tallow.** An animal fat containing  $C_{16}$  to  $C_{24}$ .

**Properties:** The solidifying points of the different tallow are as follows: from 20-45C for horse fat, 27-38C for beef tallow, 54-56C for stearin and oleo, 32-41C for mutton tallow; d 0.86; refr index 46-49 (40C) (Zeiss); iodine value 193-202; flash p 509F (265C). Combustible.

**Derivation:** Extracted from the solid fat or "suet" of cattle, sheep, or horses by dry or wet rendering.

**Chief constituents:** Stearin, palmitin, and olein.

**Grade:** Edible; inedible; beef tallow; mutton tallow; horse fat; acidless; edible, extra.

**Use:** Soap stock, leather dressing, candles, greases, manufacture of stearic and oleic acids, animal feeds, adherent in tire molds.

**tallow oil.** See "Peacock" [Pfow].

**"Tamol" [Rohm & Haas].** TM for anionic, polymer-type dispersing agents. Supplied as light-colored powders or aqueous solutions. Effective dispersant for aqueous suspensions of insoluble dyestuffs, polymers, clays, tanning agents, and pigments.

**Use:** Manufacture of dyestuff pastes, textile printing and dyeing, pigment dispersion in textile backings, latex paints and paper coatings, retanning and bleaching of leather, dye resist in leather dyeing, dispersion of pitch in paper manufacture, presfloc prevention in the manufacture of synthetic rubber.

**"Tanscol CG" [Sybron].** (isopropylhiphenyl).

**CAS:** 25640-78-2. TM for solvent.

**Use:** In carbonless-copy-paper systems, replaces PCB in capacitors, heat transfer fluid.

**"Tanak" MRX [Cytec].** TM for melamine-formaldehyde resin tanning agent used to make pure-white leather and for bleaching and filling chrome leather.

**"Tanamer" [Cytec].** TM for sodium polyacrylate adhesive for use during the drying of leather. See acrylate.

**"Tandem 552" [ACH].** TM for emulsifiers.  
**Use:** As pan release agents for frozen desserts, ice cream, baked goods; antibrowning agent for fresh-cut fruits, and vegetable.

**tangerine oil.** See citrus peel oil.

**tankage.** (animal tankage; tankage rough ammoniate). The product obtained in abattoir by-product plants from meat scraps and bones, that are boiled under pressure and allowed to settle. The grease is removed from the top and the liquor drawn off. The scrap is then pressed, dried, and sold for fertilizer.

**Grade:** Based on percentage of ammonia and bone phosphate. A medium grade has 10% ammonia and 20% bone phosphate. Concentrated tankage has had the boiled-down tank liquor and press water added to it before drying and runs 15-17% ammonia.

**Hazard:** Flammable, may ignite spontaneously.

**tankage, garbage.** (tankage fertilizer). Garbage treated with steam under pressure, the water and some of the grease removed by pressing, and further grease removed by solvent extraction. Contains 3-4% ammonia, 2-5% phosphoric acid, and 0.50-1.00% potash.

**Hazard:** Flammable, may ignite spontaneously.

**Use:** Fertilizer.

**tannic acid.** (gallotannic acid; described as a penta-(*m*-digalloyl)-glucose).

**CAS:** 1401-55-4.  $C_{28}H_{34}O_{14}$ . Natural substance widely found in nutgalls, tree barks, and other plant parts. Tannins are known to be gallic acid derivatives. A solution of tannic acid will precipitate albumin. Tannins are classified according to their behavior on dry distillation into two groups, (1) condensed tannins, which yield catechol, and (2) hydrolyzable tannins, which yield pyrogallol; (2) comprises two groups on the basis of its products of hydrolysis, glucose, and (a) ellagic acid or (b) gallic acid.

**Properties:** Lustrous, faintly yellowish, amorphous powder, glistening scales, or spongy mass; darkens on exposure to air; odorless; strong, astringent taste. Mp decomposes at 210C. Soluble in water, alcohol, and acetone; almost insoluble in benzene, chloroform, and ether. Flash p 390F (198C), autoign temp 980F (526C). Combustible.

**Derivation:** Extraction of powdered nutgalls with water and alcohol.

**Grade:** Technical, CP, NF, fluffy, FCC.

**Hazard:** Toxic by ingestion and inhalation.

**Use:** Chemicals (tannates, gallic acid, pyrogallol acid, hydrosols of the noble metals); alcohol denaturant; tanning; textiles (mordant and fixative); electroplating; galvanoplastics (gelatin precipitant); clarification agent in wine manufacture, brewing



## TANNIN

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and foods, writing inks; pharmaceuticals; deodorization of crude oil; photography; paper (sizing, mordant for colored papers); treatment of minor burns.

**tannin.** Any of a broad group of plant-derived phenolic compounds characterized by their ability to precipitate proteins. Some are more toxic than others, depending on their source. Those derived from nutgalls are believed to be carcinogens, while those found in tea and coffee may be virtually non-toxic.

See tannic acid.

**tanning.** The preservation of hides or skins by use of a chemical that (1) makes them immune to bacterial attack; (2) raises the shrinkage temperature; and (3) prevents the collagen fibers from sticking together on drying, so that the material remains porous, soft, and flexible. Vegetable tanning is used mostly for sole and heavy-duty leathers. The chief vegetable tannins are water extracts of special types of wood or bark, especially quebracho and wattle. The main active constituent is tannic acid. The tannins penetrate the skin or hides after long periods of soaking, during which the molecular aggregates of the tannin form cross-links between the polypeptide chains of the skin proteins; hydrogen bonding is an important factor.

In mineral or chrome tanning, the sulfates of chromium, aluminum, and zirconium are used (the last two for white leather); here the reaction is of a coordination nature between the carboxyl groups of the skin collagen and the metal atom. Synthas are also used; these are sulfonated phenol or naphthols condensed with formaldehyde. Condensation products other than phenol having strong hydrogen-bonding power have been developed. Tanning by any method is a time-consuming and exacting process, requiring careful control of pH, temperature, humidity, and concentration factors. For further information refer to Tanners' Council, University of Cincinnati, Cincinnati, Ohio.

See leather.

**tannic acid anhydride.** See tantalum oxide.

**tannic chloride.** See tantalum chloride.

**tantallite.**  $(\text{Fe}, \text{Hg})(\text{TaNb})_2\text{O}_6$ . The most important ore of tantalum, found in Canada, Africa, Brazil, Malaysia. When niobium content exceeds that of tantalum, the ore is called columbite.

**tantalum.**

CAS: 7440-25-7. Ta. Element of atomic number 73 in group VB of the periodic table, atw 180.9479, valences of 2, 3, 5; no stable isotopes.

**Properties:** (1) Black powder. (2) Steel-blue-colored metal when unpolished, nearly a platinum-white color when polished. D (1) 14.491, (2) 16.6 (worked metal), mp 2996C, bp 5425C, tensile strength of

drawn wire may be as high as 130,000 psi, refr index 2.05, expansion coefficients  $8 \times 10^{-4}$  over range 20-1500C. Electrical resistance 13.6 microhm-cm (0C), 32.0 (500C). Soluble in fused alkalis; insoluble in acids except hydrofluoric and fuming sulfuric acids.

**Occurrence:** Canada, Thailand, Malaysia, Brazil. **Derivation:** From tantalum potassium fluoride by heating in an electric furnace, by sodium reduction or by fused salt electrolysis. The powdered metal is converted to a massive metal by sintering in a vacuum. Foot-long crystals can be grown by arc fusion. **Corrosion resistance:** 99.5% pure tantalum is resistant to all concentrations of hot and cold sulfuric acid (except concentrated boiling), hydrochloric acid, nitric and acetic acids, hot and cold dilute sodium hydroxide, all dilutions of hot and cold ammonium hydroxide, mine and seawaters, moist sulfuric atmospheres, aqueous solutions of chlorine. **Grade:** Powder 99.5% pure, sheet, rods, wire, ultra-pure, single crystals.

**Hazard:** Dust or powder may be flammable. Toxic by inhalation. TLV: 5 mg/m<sup>3</sup>.

**Use:** Capacitors, chemical equipment, dental and surgical instruments, rectifiers, vacuum tubes, furnace components, high-speed tools, catalyst, getter alloys, sutures and body implants, electronic circuitry, thin-film components.

**tantalum alcoholate.** (pentaoxotantalum).  $(\text{C}_2\text{H}_5\text{O})_5\text{Ta}$ .

**Use:** Catalyst, intermediates for pure tantalates, preparing thin dielectric films.

**tantalum carbide.** TaC.

**Properties:** Hard, heavy, refractory, crystalline solid. Mp 3875C, bp 5500C, d 14.5, hardness 1800 kg/sq mm, resistivity 30 microhm-cm (room temperature). Extremely resistant to chemical action except at elevated temperature.

**Derivation:** Tantalum oxide and carbon heated at high temperatures.

**Use:** Cutting tools and dies, cemented carbide tools.

**tantalum chloride.** (tannic chloride; tantalum pentachloride).

CAS: 7721-01-9. TaCl<sub>5</sub>.

**Properties:** Pale-yellow, crystalline powder; highly reactive. Decomposed by moist air. D 3.7, bp 242C, mp 221C. Soluble in alcohol and potassium hydroxide solution. Keep well stoppered.

**Grade:** Technical.

**Use:** Chlorination of organic substances, intermediate, production of pure metal.

**tantalum disulfide.** TaS<sub>2</sub>.

**Properties:** Black powder or crystals. Mp above 3000C. Insoluble in water.

**Available forms:** 40-micron size.

**Use:** Solid lubricant.



**"GAF" CARBONYL IRON POWDERS**

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**Properties:** Colorless crystals. D 3.01 (15C), purities up to 99.9% gadolinium salt. Slightly soluble in hot water; more soluble in cold water.

**Use:** Cryogenic research; the selenide is used in thermoelectric generating devices.

**"GAF" Carbonyl Iron Powders**

**[International Specialty].** TM for microscopic spheres of extremely pure iron. Produced in 11 carefully controlled grades ranging in particle size from 3 to 20 microns in diameter. The iron content of some types is as high as 99.5%.

**Use:** High-frequency cores for radio, telephone, television, short-wave transmitters, radar receivers, direction finders; alloying agents; catalysts; powder metallurgy; magnetic fluids.

**Gal.** Abbreviation for galactose.

**d-galactosamine hydrochloride.** (2-amino-2-deoxy-d-galactose).

CAS: 1772-03-8.  $C_6H_{11}ClNO_5$ .

**Properties:** Crystalline solid. Mw 215.64, mp 182-185C (decomposes).

**Derivation:** Amino sugar isolated from chondroitin sulfate.

**galactose.**

CAS: 59-23-4.  $C_6H_{12}O_6$ . A monosaccharide commonly occurring in milk sugar or lactose.

**Properties:** White crystals. Mp 165-168C. Soluble in hot water and pyridine; slightly soluble in glycerol.

**Derivation:** By acid hydrolysis of lactose.

**Use:** Organic synthesis, medicine (diagnostic aid).

**d(+)-galacturonic acid.**  $COOH(CH_2O)_4CHO$ .

A major constituent of plant pectins. It exhibits mutarotation, having both an  $\alpha$  and a  $\beta$  form.

**Properties:** The  $\alpha$  form melts with decomposition at 159-160C. Soluble in water, slightly soluble in hot alcohol; insoluble in ether.

**Derivation:** Hydrolysis of pectins.

**Use:** Biochemical research.

**galena.** (galenita; lead glance).

CAS: 1314-87-0.  $PbS$ . Natural lead sulfide.

**Properties:** Lead gray in color, lead-gray streak, metallic luster, good cubic cleavage. D 7.4-7.6, Mohs hardness 2.5. Soluble in strong nitric acid, in excess of hot hydrochloric acid.

**Occurrence:** Western U.S., Canada, Africa, South America.

**Use:** Chief ore of lead, frequently recovered for the silver it sometimes contains.

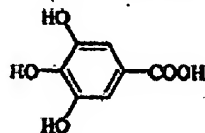
**"Galax" [Natrochem].** TM for disproportionated gum rosin or wood rosin.

**Properties:** Stable. Softening point 64-72C, acid no. 150-170 degrees.

**Use:** Adhesives, extender in rubber formulations.

**gallic acid.** (3,4,5-trihydroxybenzoic acid).

CAS: 149-91-7.  $C_6H_3(OH)_3CO_2H$ .



**Properties:** Colorless or slightly yellow crystalline needles or prisms. D 1.694, mp 222-240C. Soluble in alcohol and glycerol; sparingly soluble in water and ether.

**Derivation:** Action of mold on solutions of tannin or by boiling the latter with strong acid or caustic soda.

**Use:** Photography, writing ink, dyeing, manufacture of pyrogallol, tanning agent and manufacture of tannins, paper manufacture, pharmaceuticals, engraving and lithography, analytical reagent.

**gallium.**

CAS: 7440-55-3. Ga. Metallic element of atomic number 31, group IIIA of the periodic table, aw 69.72, valences of 2, 3; two stable isotopes.

**Properties:** Silvery-white liquid at room temperature. Mp 29.7C, bp 2403C; may be undercooled to almost 0C without solidifying, d 5.9 (25C). More dense as a liquid than as a solid. Soluble in acid, alkali; slightly soluble in mercury. Reacts with most metals at high temperatures.

**Grade:** Up to 99.9999% purity.

**Occurrence:** Prepared commercially from zinc ores and bauxite.

**Derivation:** Extraction of gallium as gallium chloride by ethyl ether or isopropyl ether and subsequent electrodeposition from an alkaline gallium oxide solution.

**Use:** The metal has no significant commercial uses. Its compounds are used as semiconductors.

**gallium antimonide.**  $GaSb$ . Available in an electronic grade.

**Use:** Semiconducting devices.

**gallium arsenide.**

CAS: 1303-00-0.  $GaAs$ .

**Properties:** Crystals. Mp 1238C. Electroluminescent in infrared light.

**Grade:** Ingots, polycrystalline form in high-purity electronic grade, single crystals. Often alloyed with gallium phosphide or indium arsenide.

**Hazard:** Toxic metal.

**Use:** Semiconductor in light-emitting diodes for telephone dials, injection lasers, solar cells, magnetoresistance devices, thermistors, microwave generation.

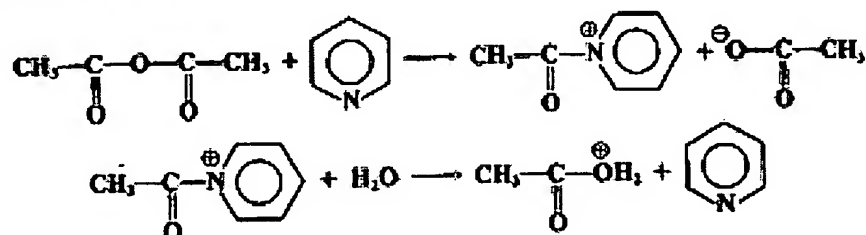
See arsenic.

**gallium oxides.** The sesquioxide,  $Ga_2O_3$ , and suboxide,  $Ga_2O$ , are known. Both are stable solids.



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successive tetrahedral mechanisms. For example, pyridine catalyzes the hydrolysis of acetic anhydride in this manner:<sup>411</sup>

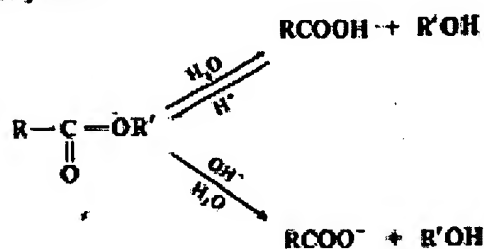


Many other nucleophiles similarly catalyze the reaction.

OS I, 408; II, 140, 368, 382; IV, 766; V, 8, 813.

## O-11 Hydrolysis of Esters

## Hydroxy-de-alkoxylation



Ester hydrolysis is usually catalyzed by acids or bases. Since OR is a much poorer leaving group than halide or OCOR, water alone does not hydrolyze most esters. When bases catalyze the reaction, the attacking species is the more powerful nucleophile OH<sup>-</sup>. This reaction is called *saponification* and gives the salt of the acid. Acids catalyze the reaction by making the carbonyl carbon more positive and therefore more susceptible to attack by the nucleophile. Both reactions are equilibrium reactions, so that they are practicable only when there is a way of shifting the equilibrium to the right. Since formation of the salt does just this, ester hydrolysis is almost always done for preparative purposes in basic solution, unless the compound is base-sensitive. Ester hydrolysis may also be catalyzed by metal ions, by enzymes, and by nucleophiles (see O-10).<sup>412</sup> Methanesulfonic acid is also a good catalyst,<sup>413</sup> as are Me<sub>2</sub>SiI<sup>414</sup> and MeSiCH<sub>3</sub>-NaI.<sup>415</sup> Phenolic esters may be similarly cleaved; in fact the reaction is usually faster for these compounds. Lactones also undergo the reaction<sup>416</sup> (though if the lactone is five- or six-membered, the hydroxy acid often spontaneously re-lactonizes) and thiol esters (RCOSR') give mercaptans R'SH. Sterically hindered esters are hydrolyzed with difficulty (p. 299), though this can be accomplished at room temperature with "anhydrous hydroxide," generated via the reaction of 2 moles of *n*-BuOK with 1 mole of water.<sup>417</sup> Hindered esters can also be cleaved with *n*-propyllithium.<sup>418</sup> For esters insoluble in water the rate

<sup>412</sup> Butler and Gold, *J. Chem. Soc.* 4362 (1961); Ferrel and Jacobs, *J. Am. Chem. Soc.* 92, 5432, 5442 (1970); Dady and Finlayson, *Aust. J. Chem.* 36, 1951 (1983).

<sup>413</sup> Loew, *Chem. Ind. (London)* 193 (1964).

<sup>414</sup> Ho and Oda, *Angew. Chem. Int. Ed. Engl.* 15, 774 (1976); *Angew. Chem.* 88, 847; Jung and Lysik, *J. Am. Chem. Soc.* 99, 968 (1977). For a review of this reagent, see Oda and Narita, *Tetrahedron* 38, 2225-2277 (1982).

<sup>415</sup> Oishi, Hasebe, Singh, and Motowara, *J. Org. Chem.* 48, 3667 (1983).

<sup>416</sup> For a review of the mechanisms of lactone hydrolysis, see Kaiser and Keady, *Prog. Biorg. Chem.* 4, 239-267 (1975), pp. 254-265.

<sup>417</sup> Cassman and Schenk, *J. Org. Chem.* 42, 918 (1977).

<sup>418</sup> Lilon, Dubois, MacPhee, and Bonzaugou, *Tetrahedron* 35, 2077 (1979).



of hydrolysis and saponification can be greatly increased by the application of ultrasound.<sup>428</sup> Phase-transfer techniques have also been applied.<sup>429</sup>

Ingold<sup>430</sup> has classified the acid- and base-catalyzed hydrolyses of esters (and the formation of esters, since these are reversible reactions and thus have the same mechanisms) into eight possible mechanisms (Table 14), depending on the following criteria: (1) acid- or base-catalyzed, (2) unimolecular or bimolecular, and (3) acyl cleavage or alkyl cleavage.<sup>431</sup> All eight of these are S<sub>N</sub>1, S<sub>N</sub>2, or tetrahedral mechanisms. The acid-catalyzed mechanisms are shown with reversible arrows. They are not only reversible but symmetrical; that is, the mechanisms for ester formation are exactly the same as for hydrolysis, except that H replaces R. Internal proton transfers, such as shown for A and B and for C and D, may not actually be direct but may take place through the solvent. There is much physical evidence to show that esters are initially protonated on the carbonyl and not on the alkyl oxygen (Chapter 8, Ref. 16). We have nevertheless shown the AAc1 mechanism as proceeding through the ether-protonated intermediate A, since it is difficult to envision OR' as a leaving group here. It is of course possible for a reaction to proceed through an intermediate even if only a tiny concentration is present. The designations AAc1, etc., are those of Ingold. The AAc2 and AAc1 mechanisms are also called A2 and A1, respectively. It may be noted that the AAc1 mechanism is actually the same as the S<sub>N</sub>1cA mechanism for this type of substrate and that AAc2 is analogous to S<sub>N</sub>2cA. Some authors use A1 and A2 to refer to all types of nucleophilic substitution in which the leaving group first acquires a proton. The base-catalyzed reactions are

TABLE 14 Classification of the eight mechanisms for ester hydrolysis and formation<sup>432</sup>

Name	Type	
Acid catalyzed	AAc1	S <sub>N</sub> 1
	AAc2	Tetrahedral
	AAc1	S <sub>N</sub> 1
	AAc2	S <sub>N</sub> 2
Acid catalyzed	Bac1	S <sub>N</sub> 1
	Bac2	Tetrahedral
Base catalyzed	Bac1	S <sub>N</sub> 1
	Bac2	S <sub>N</sub> 2

<sup>428</sup> Moon, Dackin, and Conney, *Tetrahedron Lett.* 3917 (1979).

<sup>429</sup> Dehnbach and Nairnjo, *J. Chem. Res. Synop.* 238 (1979).

<sup>430</sup> Ingold, *Ref.* 322, pp. 1129-1131.

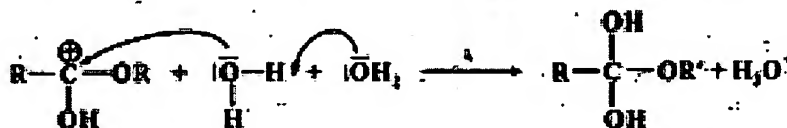
<sup>431</sup> For reviews of the mechanisms of ester hydrolysis and formation, see Kirby, in Bamford and Tipper, *Ref.* 163, vol. 10, pp. 57-207, 1972; Duranto, in Patai, *Ref.* 130, pp. 505-588.



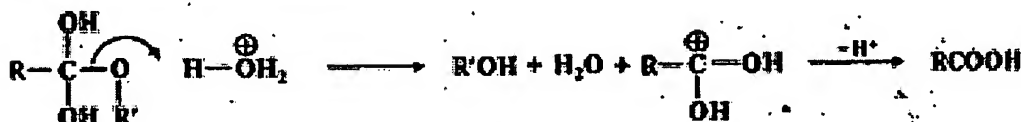
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not shown with reversible arrows, since they are reversible only in theory and not in practice. Hydrolyses taking place under neutral conditions are classified as B mechanisms.

Of the eight mechanisms, only six have actually been observed in hydrolysis of carboxylic esters. The two that have not been observed are the BAC1 and the AAL2 mechanisms. The BAC1 is an S<sub>N</sub>1 mechanism with OR' as the leaving group, which does not happen, while the AAL2 requires water to be a nucleophile in an S<sub>N</sub>2 process.<sup>42</sup> The most common mechanisms are the BAC2 for basic catalysis and the AAC2<sup>43</sup> for acid catalysis, that is, the two tetrahedral mechanisms. Both of these involve acyl-oxygen cleavage. The evidence for this is: (1) hydrolysis with H<sub>2</sub><sup>18</sup>O results in the <sup>18</sup>O appearing in the acid and not in the alcohol;<sup>41</sup> (2) esters with chiral R' groups give alcohols with retention of configuration;<sup>42</sup> (3) allylic R' gives no allylic rearrangement;<sup>42</sup> (4) neopentyl R' gives no rearrangement;<sup>44</sup> all these facts indicate that the O—R' bond is not broken. It has been concluded that two molecules of water are required in the AAC2 mechanism.



If this is so, the protonated derivatives C and D would not appear at all. This conclusion stems from a value of *w* (see p. 225) of about 5, indicating that water acts as a proton donor here as well as a nucleophile.<sup>41</sup> Termolecular processes are rare, but in this case the two water molecules are already connected by a hydrogen bond. To maintain the symmetry of the process, the reaction would then continue as follows:



The other mechanism involving acyl cleavage is the AAC1 mechanism. This is rare, being found only where R is very bulky, so that bimolecular attack is sterically hindered, and only in ionizing solvents. The mechanism has been demonstrated for esters of 2,4,6-trimethylbenzoic acid (mesitoic acid). This acid depresses the freezing point of sulfuric acid four times as much as would be predicted from its molecular weight, which is evidence for the equilibrium



In a comparable solution of benzoic acid the freezing point is depressed only twice the predicted amount, indicating only a normal acid-base reaction. Further, a sulfuric acid solution of methyl mesitoate when poured into water gave mesitoic acid, while a similar solution of methyl benzoate

<sup>42</sup>There is evidence that the AAL2 mechanism can take place in the hydrolysis of imino esters R(OH)=NR'; McClelland, *J. Am. Chem. Soc.*, **97**, 3177 (1975).

<sup>43</sup>For a discussion of this mechanism with specific attention to the proton transfers involved, see Zimmerman and Rudolph, *Angew. Chem. Int. Ed. Engl.*, **4**, 40-49 (1965) [*Angew. Chem.*, **77**, 65-74].

<sup>44</sup>For one of several examples, see Polanyi and Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934).

<sup>45</sup>Holmberg, *Ber.*, **45**, 2597 (1912).

<sup>46</sup>Ingold and Ingold, *J. Chem. Soc.*, 758 (1932).

<sup>47</sup>Norton and Quayle, *J. Am. Chem. Soc.*, **62**, 1170 (1940).

<sup>48</sup>Martin, *J. Am. Chem. Soc.*, **84**, 4130 (1962). See also Lamo, *J. Am. Chem. Soc.*, **86**, 2521 (1964); Laro, Chering, and Doney, *J. Am. Chem. Soc.*, **90**, 6692 (1968); Yama and McClelland, *J. Am. Chem. Soc.*, **89**, 2686 (1967); Yama, *Acc. Chem. Res.*, **6**, 136-144 (1971); Hoxley, Warren, and Hogg, *J. Org. Chem.*, **46**, 59 (1981).



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